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by V. B. Leonas

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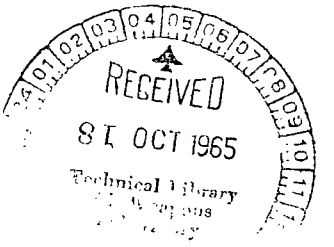

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ABSTRACT

At a higher level of sophistication than heretofore, the problem of a gas atom or diatomic molecule striking a solid surface is analyzed and calculated on a computer. A clasical mechanical model is used, representing the solid as a straight, effectively infinitely long (10 links), head-on atomic chain. The binding of the chain atoms is assumed to be either elastic coupling or a Lennard-Jones potential. The conditions for stopping, capture, and back-scattering of the incident particle are ascertained. The case when the outermost (surface) atom of the chain is an adsorbed dissimilar atom is analyzed. The results are compared with earlier data, revealing significant discrepancies.

The problem of energy exchange in the collision of a molecule (or atom) /124* with a linear atomic chain is investigated. The equations of motion is solved for the system of particles forming the linear chain and impingent molecule.

The following quantities are determined for various values of the initial energy and mass of the impingent particle: the asymptotic values of the particle velocity after collision, the threshold values of the particle capture energy (adsorption model), degree of vibrational excitation of the back-scattered particle.

There is a long history behind the attempts to account theoretically for the interaction of gas particles with the surface of a solid and the associated calculations, for example, of the accomodation coefficient; this problem has recently begun to enjoy a revival of interest (refs. 1 to 3).

In reference 4, which appears to be one of the first on the subject, the phenomenon is treated simply as the elastic collision of rigid spheres. Later on, more rigorous methods were brought into the calculations, specifically the tools of quantum mechanics. A review of the work done prior to 1938 is contained in a paper by Frenkel' (ref. 5); in that work he demonstrated the identical correspondence of the results of the classical and quantum descriptions of the interaction between heavy gas particles and a solid surface. In the concluding portion of the paper, recommendations are given for a more realistic description of the interaction between a surface and a particle striking it. It was proposed, in particular, that nonlinear terms be included in the expression for the forces of interaction of lattice atoms of the solid as well as the gas particle with the outer (surface) lattice atoms. In light of this recommendation, the following rationale for describing the effect suggests itself.

*Numbers in the margin indicate pagination in the original foreign text.

The solid is approximated by a linear chain of elastically (or otherwise) coupled, initially stationary atoms. The collision takes place along the axial line of the chain (head-on); when this happens, the impingent particle can be either an "atom"or a "molecule." The motion of the particles is described within the framework of classical mechanics; after writing the set of equations of motion for the particles and specifying the initial conditions, this system can be solved by computer techniques.

Figure 1 shows the system of particles under consideration, as well as the notation convention used to designate the forces acting between them. The

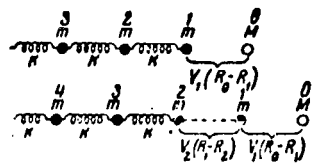

Figure 1

interaction of the first two particles, numbered 0 and 1, of the upper chain is described by the Lennard-Jones potential:

$$V_1 = 4\varepsilon_1\left[\left(\frac{\sigma}{R_0 - R_1}\right)^{12} - \left(\frac{\sigma}{R_0 - R_1}\right)^{6}\right] \tag{1}$$

and the atoms of the chain are connected by the elastic forces

$$V = K(R_i - R_{i+1})^2 \tag{2}$$

(the numbering of the particles is given in figure 1; ϵ_1 and σ are the potential parameters, K is the elastic constant of the chain). For the lower chain, the interaction of the first and second (1, 2) atoms of the chain is described by the potential

$$V_2 = 4\varepsilon_2\left[\left(\frac{\sigma}{R_1 - R_2}\right)^{12} - \left(\frac{\sigma}{R_1 - R_2}\right)^{6}\right] \tag{3}$$

These particle systems enable us, by variation of the initial conditions and forces, to analyze the following special problems: a) the collision of an atom with a uniform chain of elastically coupled atoms; b) collision with a nonuniform chain (simulating collision via an adsorbed atom); c) head-on collision of a nonrotating vibrationally excited and a nonexcited diatomic molecule

with a linear uniform chain. We write the equations of motion for the particles in a coordinate system rigidly attached to the initial position of the chain:

$$\begin{aligned}
M\frac{d^2R_0}{dt^2} &= -\frac{dV_1(R_0-R_1)}{d(R_0-R_1)}\\
m_1\frac{d^2R_1}{dt^2} &= -\frac{dV_2(R_1-R_2)}{d(R_1-R_2)}+\frac{dV_1(R_0-R_1)}{d(R_0-R_1)}\\
m_2\frac{d^2R_2}{dt^2} &= \frac{dV_2(R_1-R_2)}{d(R_1-R_2)}-K(R_2-R_3)\\
&\cdots\cdots\cdots\cdots\cdots\\
m\frac{d^2R_j}{dt^2} &= K(R_{j-1}-2R_j+R_{j+1})
\end{aligned} \qquad (4)$$

Here M, m_1, m are the masses of the particles (fig. 1), j is the number of atoms in the chain and is chosen equal to ten. Below, we consider collisions unaccompanied by capture, so that for j = 10 the chain turns out to be equivalent to a chain of infinite length, since the perturbation cannot propagate to the distant atoms within the period of interaction. /125

The set of equations (4) reduces to a set of first-order equations (ref. 2) containing the parameters

$$\mu_1=\frac{M}{m},\quad \mu_2=\frac{m_1}{m},\quad \alpha_1=\frac{\varepsilon_1}{K\underline{1}^2},\quad \alpha_2=\frac{\varepsilon_2}{K\underline{1}^2} \qquad (5)$$

The parameter $\underline{1}$ gives the initial energy of the impingent particle:

$$E_0=\tfrac{1}{2}Mu_0^2\ (E_0=\tfrac{1}{4}\varepsilon_1)$$

The dimensionless parameters $\alpha_{1,2}$ were set equal to 10^{-2} - 10^{-3} or 1, corresponding to van der Waals bonds in the former case and to the interatomic bonds in the molecule or crystal in the latter; the lattice constant $\underline{a}$ was chosen equal to σ in the Lennard-Jones potential, a step that is justified by the real values of these parameters. Electronic computer equipment was used to solve the set of equations numerically for different values of the parameters μ, $\underline{1}$, α.

In discussing the results, we first note that it would obviously be unreasonable to demand that the analytic model yield the true values of the parameters, such as the accommodation coefficient; rather, we are looking at this point for indications as to the nature of the interaction, the influence of the controlling parameters, the dynamics of the collision, etc. The numerical values of these quantities have to be obtained by the simpler and more reliable expedient of experiments performed under suitable conditions.

Two variants were used in the analysis of an atom striking the stationary chain: in the first variant, the outermost atom was assumed to be coupled elastically with its neighbor (upper chain, fig. 1), in the second variant (lower chain, fig. 1) this coupling was described by the Lennard-Jones potential ($\alpha_2 = 1$).

The collision dynamics for the case $\alpha_2 = 1$, $\mu_2 = 1$, $\mu_1 = 0.5$ is illustrated by the typical curve shown in figure 2 for the velocity of the impingent and target particles as a function of time ($E_0 = 2.5$, 12.5, and $25\epsilon_1$).

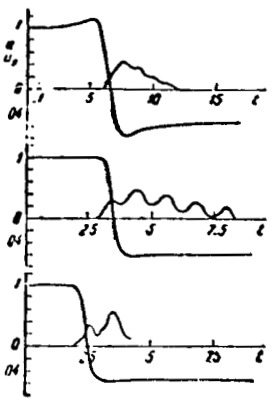

Figure 2

The time is plotted on the horizontal axis (in units of σ/u_0), the reduced instantaneous velocity (u/u_0) on the vertical axis; the upper half-plane corresponds to velocities directed toward the chain, the lower half-plane to velocities directed away from the chain.

The heavy solid curve gives the time dependence of the velocity for the striking (first) particle, the fine thin curve is for the struck particle.

An analysis of this kind of data leads to the following conclusions. In the case when the outermost atom is elastically coupled, for impact between particles with a reduced mass $\mu_1 = 0.1$, 0.5 and an initial energy E_0 no greater than $0.25\epsilon_1$ and $2.5\epsilon_1$, respectively, capture of the impingent particle takes place. Consequently, the critical capture energy E' slightly exceeds $0.25\epsilon_1$ and $2.5\epsilon_1$, respectively. For $\mu_1 = 1$, i.e., with equal masses for the impingent particle and outermost atom of the chain, capture of the impingent will almost always occur. As the energy of the impingent particle is increased above the critical capture value, the interaction gradually changes over to the corresponding pairwise elastic collision of the particles. The dependence of the accommodation coefficient α on the parameter $\frac{1}{\mu_1}$, which represents the reduced initial energy of the impingent particle ($\mu_1 = 0.4$), is given in figure 3, showing the transition mentioned above.

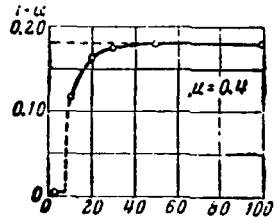

Figure 3

In the case when the coupling of the outermost atom with the chain is described by the Lennard-Jones potential ($\alpha_3 = 1$), significant departures from the dependences described above are observed. For instance, the critical capture energies are greatly reduced and, as an example, for $\mu_1 = 0.95$ capture only occurs when $E_0 \leq 2.5\epsilon_1$; for $\mu_1 = 0.1$ and $E_0 \geq 1.25\epsilon_1$, pairwise elastic collision occurs, whereas for $\mu_1 = 0.5$ and $E_0 \geq 2.5\epsilon_1$, the final velocity of the back-scattered particle considerably exceeds the value for elastic collision of rigid spheres of the same mass (fig. 2). From this it may be concluded that the nature of the forces binding the atoms in the chain has a very strong influence on the behavior of the energy exchange in collision. /126

The results of the calculations for the model of an "adsorbed" outermost atom (lower chain of figure 1 with $\alpha_1 = 10^{-1}$, $\alpha_2 = 10^{-3}$ or $\alpha_2 = 10^{-2}$) show that for $\mu_1 < \mu_2$ and sufficiently high energies, the collision is elastic, whereas for $\mu_1 = \mu_2$, instead of the impingent atom being stopped and captured, it is reflected with a fairly high velocity ($\sim 0.3u_0$ for $E_0 \geq 25\epsilon_2$). The calculations also demonstrate the possible "stripping" of the adsorbed atom and capture of the impingent atom.

A comparison of these results with data obtained analytically for a similar model (refs. 2 and 3) brings out important differences in the results. First, extrapolation of the results of reference 2 and 3 to large initial energies leads to values for the losses different from those corresponding to pairwise elastic collision (see fig. 3 of ref. 2). Second, reference 2 gives the following numerical values for the critical initial energies below which particle capture should occur: $E' = 0.01\epsilon_1$ for $\mu_1 = 0.1$, $E' = 2.39\epsilon_1$ for $\mu_1 = 0.5$, $E' = 24.5\epsilon_1$ for $\mu_1 = 1$. The results of our own calculations show that these critical values do not describe the capture process; for example, for $\mu_1 = 0.5$, 0.4 and E_0 equal to $2.5\epsilon_1$ and $3.5\epsilon_1$, respectively, capture still occurs. For $\mu_1 = 1$ and $\mu_1 = 0.9$, capture takes place for essentially any value of the initial energy if the atoms of the chain are elastically coupled. Finally, if we compare figure 3 of the present paper with figure 10 of reference 3, it is apparent that in references 2 and 3 the accommodation coefficient becomes constant for very small (~ 2 for $\mu_1 = 0.4$) values of 1; this is also incompatible with the results obtained herein.

Summarizing the result obtained, the following is evident. For the model under study, the effectiveness of the energy exchange in collision with relative energies exceeding the energy of physical adsorption (ϵ_1) is determined in the main by the nature of the forces acting between the atoms of the chain and depends only slightly on the form of the potential curve of interaction between the impingent and outermost chain atom (although the critical capture energy is sensitive to the form of the curve). The discrepancy in the results for the first and second variants suggests the possibility that the energy (or momentum) imparted to the target can be significantly reduced by comparison with the value for pairwise elastic collision.

Consider now the collision of a vibrational unperturbed nonrotating diatomic molecule with a linear chain of atoms. This problem is of possible interest in connection with the following.

The experimental determination of the energy losses in a number of cases presupposes the possibility of neglecting the internal degrees of freedom. The results of a calculation for the most favorable case of a head-on collision gives an estimate of the permissibility of this neglect. Moreover, in the literature dealing with the theoretical analysis of collision between particles and a solid surface, there is an almost total lack of papers in which molecular collision is considered. The only paper (ref. 6) treating this problem is mainly concerned with an investigation of the statistical problem of relaxation of the internal degrees of freedom in the capture of molecules by the surface. A suitable calculation would provide an estimate of the contribution from the internal degrees of freedom to the energy exchange in collision, as well as a means for investigating the collision dynamics.

In the scheme under consideration, a molecule is "produced" by situating two atoms (fig. 1) at a distance such that the forces of mutual attraction and repulsion just cancel one another (dissociation energy equal to $\epsilon_1 = 100\epsilon_2$). Thus bound, the atoms have imparted to them a velocity u_0 (where $\frac{1}{2}Mu_0^2 = \frac{1}{4}\epsilon_2$) /127 directed toward the chain; our task is to trace the variation of the velocities of the atoms in the molecule with time. The following values are assigned to the parameters

$$\alpha_1 = 1, \quad \alpha_2 = 10^{-4},$$
$$\mu_1 = \mu_2 = 0.2,\ 0.45, \quad l = 3 + 5000$$

The results of the calculation are shown in figure 4 (using the same notation as before); the heavy curve corresponds to the atom of the molecule nearest the chain, the thin line to the atom farthest from the chain. The dependence of the relative values of the total residual energy (E_1/E_0) and energy given over to the vibrational mode (E_2/E_0) on the parameter 1/100 ($\mu_1 = 0.2$) is shown in figure 5 (the scale for E_2/E_0 is reduced by 1/2).

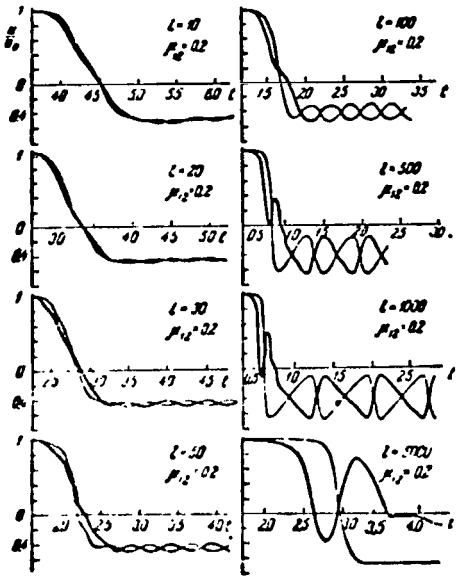

Figure 4

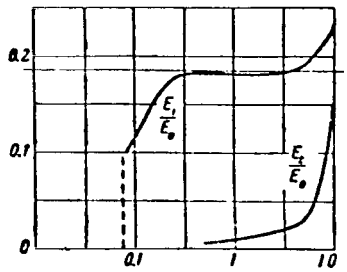

Figure 5

As evident from figure 5, up to initial energies E_0 of the order $0.01\epsilon_1$, the impingent molecule is captured. Beyond this limit the energy loss approaches the value corresponding to pairwise elastic collision, i.e., the thin curve of figure 5. The gain in vibrational energy rises steeply, beginning with $E_0 = 2.5\epsilon_1$. Dissociation does not set in until $E_0 \sim 15\epsilon_1$.

The calculation for $\mu_1 = 0.45$ predicts capture of the molecule for all initial energy values. The results imply the following conclusions.

The total energy loss in the collision of a molecule of moderate velocity ($E_0 \sim \epsilon_1$) with a linear chain closely corresponds to elastic impact of a structureless (e.g., spherical) particle of the same mass; the deviation from this value increases somewhat as the energy of the incident molecule increases.

The vibrational energy acquired by the back-scattered molecule in collision increases substantially, beginning with an initial energy $\sim \epsilon_1$. The frequency of the vibrations, as expected for an anharmonic oscillator, diminishes somewhat with increasing energy. The results indicate that excitation of the internal degrees of freedom of the molecule only slightly affects the transfer of momentum (and, hence, the resistance under conditions of molecular free flow), whereas the exchange of energy (accommodation coefficient) is more sensitive to the excitation.

The results of the computations show that in the energy range of practical interest, the influence of the vibrational degrees of freedom of molecules on the energy exchange proves to be quite small. In this case, the internal degrees of freedom do not provide a sufficiently effective energy sink and need not be taken into account, for instance in determining the energy balance of rapidly moving bodies in a severely rarefied atmosphere.

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